

Atmospheric Electron Induced X-Ray Spectrometer (AEXS) Development

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Abstract—The progress in the development of the Atmospheric Electron X-ray Spectrometer (AEXS) is described. The AEXS is a surface analysis tool based on excitation of characteristic x-ray fluorescence (XRF) spectra from samples in ambient atmospheres using a focused electron beam. Operation in ambient atmospheres with moderate-to-high spatial resolution in comparison to similar instruments is obtained through the use of a thin electron transmissive membrane to isolate the vacuum of the electron probe, obviating the need for the samples to be drawn into the probe vacuum. Our initial setup consisted of an actively pumped chamber from within which the electrons were transmitted - not a portable instrument. The instrument that has been assembled and used to acquire XRF spectra in our laboratory during the past two years consists of a 20keV electron tube sealed with a SiN membrane and requires no active pumping - a big step towards the development of a stand-alone instrument. The microprobe was used to perform elemental analysis of NIST and USGS standards, with good agreement with the certified composition for samples in up to about 90 Torr-cm thick atmosphere, and for resolving the composition of mm-sized mineral grains in inhomogeneous samples, a big improvement over the several cm-scale spatial resolution of the APXS instrument that flew on NASA's MER mission.¹²

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1. INTRODUCTION

This paper extends the work reported at previous IEEE Aerospace conferences where the concept and progress in the development of the Atmospheric Electron X-ray Spectrometer (AEXS) was described.^[1-5] The AEXS is a miniature instrument enabling rapid elemental analysis of samples on planetary surfaces *in situ* by energy dispersive analysis of x-ray fluorescence (XRF) spectra excited by a focused electron beam. The viability of a vacuum-isolation membrane for the AEXS instrument has been demonstrated under the NASA's '98 PIDDP funding, the investigation of the ability of the electron beam to excite and analyze both X-ray and electron-induced luminescence (Cathodo-Luminescence, CL) spectra has been funded by NASA's '02 ASTID program. The development of a stand-alone, vacuum-isolated instrument has been funded by NASA's '04 MIDP program. In this paper, we describe our progress in the development of the AEXS instrument, both hardware and demonstration of the AEXS capability through XRF data acquisition using textured mineral samples.

Electron beam excited energy dispersive X-ray analysis is a widely accepted technique for determining the surface elemental composition, however it has not been previously used for analysis of samples in the ambient atmosphere due to the difficulty of generating and transmitting electron

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beams through the atmosphere. The enabling component for operation in ambient atmospheres is a thin electron-transmissive membrane that isolates the vacuum of the electron source from the ambient pressure. When used with a sufficiently short membrane-to-sample working distance, the transmitted electrons impinge on samples in the external atmosphere exciting XRF spectra that are analyzed to determine surface elemental composition. The electron excitation using the AEXS is similar to that used in

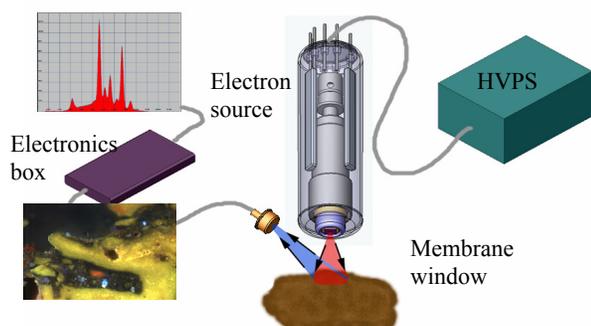


Fig. 1. The AEXS instrument concept. The AEXS consists of a miniature, vacuum-encapsulated electron source, a high-voltage power supply, and XRF detector. The high energy (>15 keV) electron beam is transmitted through an electron-transmissive vacuum-isolation membrane into the ambient atmosphere to strike the sample, exciting characteristic XRF spectra for elemental analysis of the irradiated spot. The spot area can be adjusted from sub-millimeter to several centimeter size by changing the membrane-sample working distance. In the flight prototype AEXS, the electron source and XRF detector will be integrated in a miniature instrument head. The head will be incorporated onto the rover arm, and the miniature power source and electronics placed inside the rover's warm box.

Scanning Electron Microscopy (SEM), with one significant advantage. Unlike the case in an SEM, the vacuum isolation of our electron source obviates the need for the sample to be drawn into the vacuum of the electron column. The probe requires no external pumping or sample manipulation. The spectra can be acquired from samples in their pristine state, since electron-ionization of the ambient atmosphere ensures a return current path so that nonconductive samples do not need to be coated with conductive material to prevent charging effects.

Two methods are currently available for analyzing samples at near-atmospheric pressure using electron beams. The AEXS, and the Environmental SEM (ESEM^[5]), which employs a series of pressure-limiting apertures with pumping stages to isolate the electron source vacuum from the pressure in the sample chamber. Both approaches provide rapid analysis times, and evaluation of both insulating and conducting samples is possible due to the charge neutralization provided by the current return path. The reason why we selected the membrane isolation approach is because of its amenability to developing a more compact, low mass instrument suitable for *in situ* observations for NASA missions. Although commercially

available^[6] ESEM systems permit a smaller spot size than the AEXS, the requirements for active vacuum pumping of multiple stages and the need to manipulate the inspected samples require an elaborate vacuum system resulting in a much less portable instrument than could be obtained with a vacuum-isolated microprobe. The use of thin vacuum-isolation membranes has been advocated in the past for the development of an atmospheric SEM,^[7,8] and transmission windows with various types of membranes have been implemented to construct devices for electron beam charging of small particles and subsequent electrostatic deflection,^[9] and for high-energy electron beam irradiation of surfaces and bulk materials for microbial reduction.^[10]

The AEXS instrument has been developed in several stages, consisting of demonstrating capabilities for increasingly integrated vacuum setups. The first setup^[1] demonstrated the ability of the transmitted electrons to excite XRF spectra from a pure Ti sample in the outside, 760 Torr pressure Earth atmosphere. The setup consisted of an actively pumped vacuum chamber with a 10 keV electron gun incorporated into a high vacuum feed-through at one end, and a SiN window integrated into the vacuum flange at the opposite end. The membrane was a low-stress 200 nm thick Silicon Nitride (SiN) film that bridged a 1.5 mm × 1.5 mm opening created within a Silicon (Si) substrate using standard photolithographic techniques. The Si frame was attached to a stainless steel flange using Epotech (Epoxy Technology, MA) H20E silver epoxy.^[1] The next setup² had the membrane attached directly to the exit aperture of a commercially available 10 keV gun. The gun, operated under the support of a high vacuum pump via an exhaust port, was used to excite XRF spectra from metal and mineral samples that were compared with spectra acquired within the SEM.^[3]

The most recently constructed breadboard instrument consists of a “stand-alone” microprobe with the electron-optics column encapsulated within a glass envelope sealed with a specially designed glass-tube attachment that incorporates the transmissive membrane. The microprobe differs from the previous setups in that it requires no active pumping, so that it can be used to construct a portable instrument. The electrons transmitted through the membrane excite XRF spectra that are acquired and analyzed by using an Energy-Dispersive X-ray (EDX) detection system. The microprobe and the XRF detector were put into an environmental chamber, which has been specially constructed to simulate the effect of reduced atmosphere pressure on the acquired spectra. The microprobe was calibrated and used to excite XRF spectra from a number of metal and mineral standards of known composition. In another set of experiments, a new environmental chamber was constructed and a moving stage was incorporated into it. Rock samples containing mm-scale size mineral grains of unknown composition were placed on top of the moving stage. By moving the samples underneath the electron beam, regions with different elemental abundance on the sample surface were differentiated with ~ 1.5 mm spatial resolution,

a big improvement over a several cm-scale spatial resolution of the APXS instrument on MER. The electron induced x-ray generation is very efficient, using a 1 μ A beam, the spectra were resolved with the analysis time set at 100 seconds (the same as our standard procedure in our SEM lab).

2. ENCAPSULATED MICROPROBE

The stand-alone microprobe is shown in Fig. 2. The microprobe used a Thomas Electronics^[11] electron tube (#70-1368-A) rated for operation up to 20kV. Similar to the previous tubes, the 20keV tube consists from a thermionic emitter and an electrostatic optics column to focus and accelerate the electrons. The tube is sealed using a Kovar/Pyrex/Si attachment to vacuum-isolate a glass envelope for the electron optics column.

In our early work with the 10keV tube,^{2,3} the Si chip was bonded directly to the glass tube, resulting in a large mismatch in the Coefficient of Thermal Expansion (CTE) between the lead-glass (L-29) envelope and the Si chip. The mismatch could impart large stresses during the thermal processing required for gun encapsulation and evacuation, and subsequent field use. To alleviate the CTE mismatch we later fabricated a CTE-graded seal consisting of a glass transition region with a progressively graded CTE's from the soft L-29 glass to Si, leading to an improved mechanical robustness over the epoxy process. For the 20keV tube, we were able (instead of resorting to a CTE graded seal

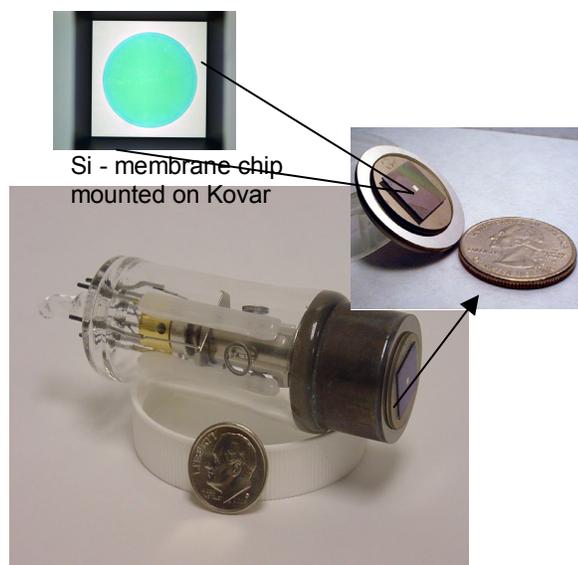


Figure 2. Vacuum-Isolated Thomas Electronics 20keV Electron gun

transition region) to specify the glass materials to be CTE-matched to Si. The electron gun is mounted on a 7052 glass stem containing an evacuation port. A commercially available 7052 glass-to-Kovar transition sleeve is glass-blown to the stem/gun subassembly. In a separate process, the Si chip is anodically bonded to a Kovar disc (see the

inset in Figure 1). The assembly process is completed by laser welding the Kovar sleeve to the Kovar disc-Si chip subassembly. Following the welding, the electron gun is evacuated, baked out at 375 deg C and vacuum processed to a final pressure in the 10^{-8} Torr range, and the evacuation port is “pinched-off” by flame sealing the exhaust tubing, creating a stand-alone vacuum-sealed electron source.

Whereas the 10keV tubes were sealed with 200 nm thick membranes, the 20keV guns are sealed with 500 nm thick membranes. One advantage of using 20keV instead of 10keV electrons is that more energetic electrons excite characteristic XRF from K_{α} lines of heavier elements, and allow using thicker membranes without any adverse effect on electron transmission from the tube. The membrane is robust enough to withstand the pressure differential yet thin enough to efficiently transmit the electrons. The membrane, a low-stress SiN film is grown on a Si substrate using low pressure chemical vapor (CVD) deposition under non-stoichiometric, silane rich conditions to produce a low tensile stress, pinhole free film on both sides of a 400 μ m thick Si wafer. By using standard photolithography and reactive ion (RIE) and wet chemical etching techniques, window openings are defined in the wafer, resulting in membrane-bridged openings within the Si support frame.

The SiN membranes are defined within $(1.5 \text{ mm})^2$ rectangular openings within the Si wafer.¹ It has been our experience that stress in the membrane tends to concentrate in corner regions of the rectangular openings thus degrading the membrane robustness. To increase the membrane robustness, some of the membranes used in later stages of our project were prepared using a JPL-pioneered micro-fabrication process¹² designed to produce “dual thickness” windows. Using his process, a thin circular central region is defined within a thicker surrounding SiN region, thus alleviating the stress in the corners of the rectangular openings. For the present application, the thickness of the circular and thicker surrounding region was 500 nm and 1 μ m, respectively. By comparing the membrane yield, the “dual thickness” windows had slightly increased robustness over the “single-thickness” windows, however a greater factor for improved robustness was due to the increased membrane thickness, from 200 nm to 500nm. A series of experiments determined that the 500 nm membranes have high electron transmission ($> 90\%$ for 20keV electrons), yet are strong enough to support up to one atmosphere differential pressure while maintaining a high vacuum within an electron column.^[1-3]

3. THE EFFECT OF THE MEMBRANE AND EXTERNAL ATMOSPHERE ON SPATIAL RESOLUTION

The effect of the membrane and the external atmosphere on the transmitted beam was investigated in detail due to its critical role for the operation of the AEXS instrument. The beam properties are modified due to electron interaction

with the traversed medium. Electrons colliding with molecules of the traversed medium scatter (Coulomb collisions) causing beam spreading, and together with energy attenuation along the electron's path will bring about energy dispersion for the transmitted beam. The physics of the interaction depends on electron energy and membrane material, and on composition and pressure of the traversed atmosphere. Beam characterization experiments were conducted within an SEM and in the outside atmosphere consisting from measurements of electron transmission and beam spreading, modeling of the effect of electron

interaction with the membrane and the outside atmosphere using Monte Carlo simulations, and comparing the predictions with experimental data. XRF spectra excited from samples in vacuum and in an environmental chamber at various pressure were measured.

The details of these studies were described previously.^[3] The main results are summarized in Figures 3 and 4 for 20 keV and 50 keV electrons. Figure 3a shows that the transmissivity exceeds 90 % for all working distances less than 10 cm. Figures 3b and 3c show the simulated scattering and beam shape for (an originally pencil-thin) beam at a 1 cm working distance. The simulated shape

is fitted to a good approximation by a Gaussian (standard deviation $\sigma = 0.4$ cm in Figure 3c). The simulated widths are compared with experimental values obtained using XRF spectra acquisition in knife-edge type experiments in SEM in Figure 4 as a function of the working. By fitting the experimental beam shapes with Gaussians, the standard deviation varied from about 0.6 mm to 1.8 mm when the membrane-target distance varied from 2.5 mm to 8 mm. Note that the experimental values are somewhat less (by about 20% to 40%) than the simulated values, however the dependence on the working distance is the same – the spot size increases with increased working distance (at least up to 10 cm distance). The predicted spot size (defined as equal twice the standard deviation) is about 6 mm at 1 cm working distance and 6 cm 10 cm working distance, for 20kV electrons at 7 Torr pressure.

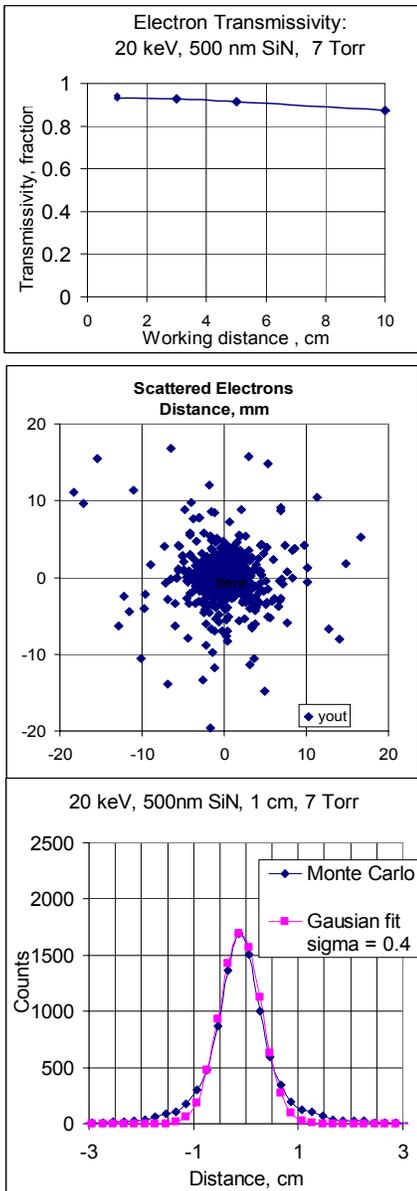


Figure 3. The Monte-Carlo simulated (a) electron transmissivity through a 500nm thick SiN membrane as a function of the membrane-sample working distance, (b) scattered electrons, and (c) electron beam shape at a 1 cm working distance is fitted by a Gaussian.

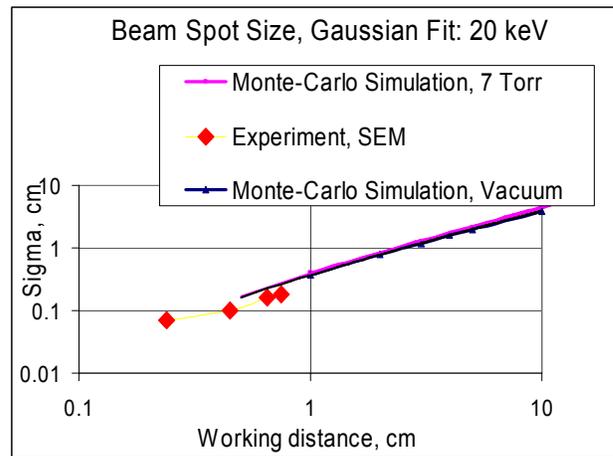


Figure 4. The beam width determined from XRF measurements in SEM. The XRF data was excited by a transmitted 20 keV beam through the 500 nm membrane, from a GaAs wafer half-coated with Cu and translated underneath the membrane in the perpendicular direction to the Cu edge. The data (diamonds) are compared to simulations (in vacuum and 7 Torr pressure) as a function of the membrane-sample working distance.

The validated model gives us confidence to predict¹² achievable spatial resolution for other values of electron energy, membrane and atmosphere thickness. Specifically, Figure 5 predicts that for 50keV electrons transmitted through a 500 nm membrane, beam spreading will be about 50% less than for the 20keV electrons, ie the transmitted beam size will be 4 mm (compared to 8 mm for 20keV beam) at 1 cm working distance. Using a thicker membrane will improve robustness of the encapsulation process. Figure 5 shows that the beam size will be the same for both the 50keV beam transmitted through a 2 μ m membrane, and 20 keV beam transmitted through a 500 nm membrane.

4. XRF SPECTRA ACQUISITION: CALIBRATION

The spectral fidelity depends on a number of factors, such as the electron energy, beam current, chemistry and pressure of the outside atmosphere, the relative positions and orientation of the electron source, sample and X-ray detector, and the detector spectral resolution. To study the effect of atmosphere pressure, an environmental chamber has been assembled to house the 20 keV gun, XRF detector and interrogated samples, with the ability to control the content and pressure (from low vacuum levels, 10^{-4} Torr or regulating to a higher pressure) of the atmosphere. The chamber was used to detect XRF spectra for a number of metal NIST (National Institute of Standards and Technology) samples as well as for a number of more complex mineral powder USGS (US Geological Survey) standards at various atmosphere thickness. Good agreement with the provider-certified compositions was obtained up to about 90 Torr-cm thick atmosphere in the chamber.

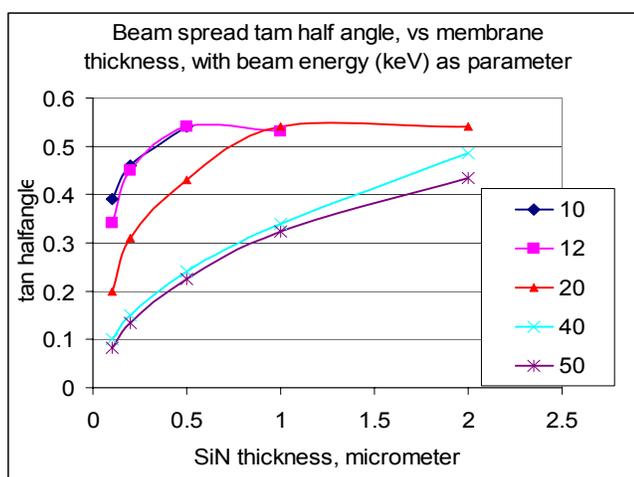


Figure 5. Monte-Carlo simulated^[13] beam angular spreading as a function of the membrane thickness. The beam size (in cm) for different working distance can be obtained by multiplying the beam spread tangent (plotted) by the working distance.

Figure 6 shows the acquired spectra for a BCR-2 (Basalt, Columbia River) sample for a set of Nitrogen pressures varying from 10^{-4} Torr to 200 Torr. Energy dispersive analysis of XRF spectra is performed by using miniature solid-state detectors that determine the height of current pulses resulting from the X-rays collected by the detector. The spectra in Figure 6 were acquired by using a Peltier-cooled, low-noise *p type-intrinsic-n type* (PIN) diode detector manufactured by Amptek Inc.¹⁵ (Model #XR-100CR, electronics #PX2CR) that was used on the Mars Pathfinder APXS¹⁶ instrument. The energy scale of the acquired data was calibrated by using an Am X-ray fluorescing source. The detector's Full-Width-Half-Maximum (FWHM) is 253 eV@5.9 keV, the pulse shaping pulse time is 12 μ sec. The detector aperture (13 mm² area) is sealed with a 12 μ m thick Be window, which effectively cuts off low energy lines (below about 1.2 keV) from reaching the detector active region. Care was exercised so that no Si lines generated by electron interaction with the membrane and the Si support frame reach the detector. The

electron gun and detector were positioned in the chamber in the same plane with their axes mirrored and pointing to the sample at about 20 degrees from the normal direction to the sample (take-off angle 70 degrees). The membrane-to-sample working distance was about 1 cm. For the sample-to-detector distance of about 3 cm, the spectra acquisition time required to resolve the XRF spectra was set to 100 seconds of detector live time using a 1 μ A beam current.

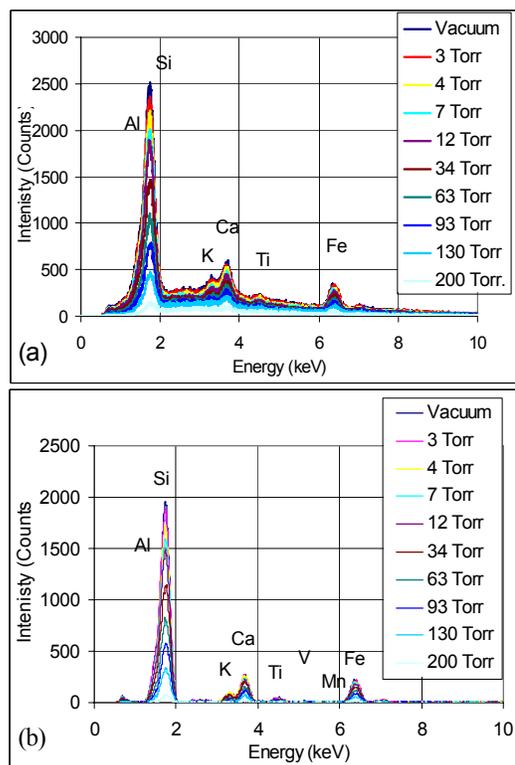


Figure 6. XRF spectra for the BCR-2 (Basalt, Columbia River) mineral samples taken using the vacuum-isolated 20keV electron gun in the environmental chamber at several values of the ambient pressure: (a) with background, (b) subtracted background. (The spectra are shown in the order of increase pressure, with the vacuum at top).

Figure 6a shows the acquired spectra before the subtraction of the Bremsstrahlung radiation background. The spectra were analyzed using a commercially available EDX Quantification software acquired from IXRF corporation,^[17] and used by many laboratory SEM systems^[18] to determine the elemental abundance by energy dispersive analysis of electron-excited XRF spectra. Upon the specification of the beam energy and take-off angle, and specifying the elements list for the analysis, the software calculates the required line energies and resolutions for the specified analyte lines, subtracts the best-fit Bremsstrahlung background, and determines the elemental abundance by using Gaussian deconvolution for peak extraction and ZAF corrections for the quantitative analysis.^[14,17] In our experiments, the abundances were determined by performing "standard-less" quantification. That is, no side-by-side standards were

provided for additional calibration measurements. The results of the measurements using samples with known composition (i.e. traceable standards) establish limits on the instrument's performance. Figure 6b shows the spectra after the subtraction of the Bremsstrahlung background. The computed elemental abundance is listed in Table 1, together with the provider-certified composition.^[19] The agreement between the determined and certified abundances is good.

Table 1 lists the certified^[19] and the experimentally determined composition (in weight %,) for the BCR-2 sample up to 200 Torr-cm thick atmosphere in the chamber for all analyzed elements, including the abundant elements (Si, Fe, Al and Ca, with K_{α} lines well above the detection cutoff of the Be- window), light elements (Na, Mg, with K_{α} lines near the Be-window cutoff), less abundant elements (K and Ti at 1.5 %), and trace elements (Mn, P, Ba, and V, with less than .15 % abundance). By comparing the certified and determined composition for elements other than the light elements, the detection limit was about 1 %, similar to that obtained in SEM. Si, Fe, Al and Ca were detected at all pressures. Ti and K were also detected, albeit with a large relative error at some pressures.

Table 1 lists the absolute abundance, the relative error is obtained as the normalized difference between the certified and determined abundances. The relative errors were generally larger for trace and light elements than for more abundant elements. The trace elements (TR) were detected in some but not all cases. For the light elements, the K_{α} lines (at 1.041 keV and 1.254 keV for Na and Mg, respectively) are effectively cut-off (CF) from detection due to strong attenuation by the 12 μ m thick Be window of the Amptek detector. The "undetectables" (mostly Oxygen, since the elements are present as oxides) comprise about 46% of the BCR-2 sample by weight. Note that (for the

detectable elements) the difference between the certified and derived abundance increased with increasing pressure; the absolute difference was as large as 5% (of weight) for Fe, and less for other elements, at pressures up to about 90 Torr.

5. THE EFFECT OF EXTERNAL ATMOSPHERE ON QUANTITATIVE EDX ANALYSIS

As Table 1 shows, the agreement between the determined and certified abundance is good up to about 90 Torr Nitrogen pressure. At higher atmosphere thickness, the discrepancy between the certified and experimental abundance becomes greater than 50% for most of the analyzed elements. The disagreement was traced to the neglect by the EDX software of the effect of atmosphere and membrane on the analysis.

Several factors were not taken into account during the EDX analysis that could improve accuracy of the analysis at higher pressure. The EDX software assumes that the examined samples are probed using a monochromatic electron beam in vacuum. However, unlike SEM, the excitation beam using AEXS is not monochromatic (due to energy dispersion caused by electron interaction with the membrane and the atmosphere). The EDX software simulates the escape probability of the excited XRF into vacuum, however the X-rays excited using the AEXS are attenuated by the external atmosphere as they travel between the sample and the detector.

The most striking feature in Figure 6 is the decrease in the height of the spectral peaks at increased pressure. Figure 7 plots the number of the X-ray counts associated with the four strongest peaks (Si, Fe, Ca, Al) versus pressure. Notice

Table 1. Elemental abundance of BCR-2 sample vs pressure: Comparison with the certified composition. CF = elements with the characteristic X-ray energy near the detector Be window cut-off energy. TR = trace element below the detection limit

Composition, Weight, %											
Element		Certifd	Vac	3 Torr	7 Torr	12 Torr	34 Torr	63 Torr	94 Torr	130 Torr	200 Torr
Si	Detected	25.3	28.89	28.56	28.95	28.45	26.68	27.11	26.00	23.23	17.28
Fe	"	9.65	12.07	11.52	12.30	12.69	13.14	14.08	14.88	17.25	23.18
Al	"	7.14	6.10	6.57	5.93	5.74	5.12	4.44	3.57	3.30	0.72
Ca	"	5.09	4.85	5.10	5.30	5.18	6.53	6.29	6.77	6.87	6.38
K	"	1.49	1.56	1.81	1.24	1.21	2.35	1.21	1.26	0.88	0.87
Ti	"	1.35	1.19	1.14	0.89	1.21	0.81	1.30	1.18	1.41	1.43
Na	NC	2.34	0.03	0.03	0.00	0.00	0.00	0.07	0.04	0.00	0.00
Mg	"	2.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.13
Mn	TR	0.152	0.12	0.11	0.18	0.24	0.13	0.24	0.24	0.89	1.47
P	"	0.15	0.00	0.00	0.00	0.01	0.00	0.09	0.40	0.61	1.03
Ba	"	0.0683	0.00	0.00	0.00	0.20	0.00	0.00	0.44	0.00	1.22
V	"	0.0416	0.13	0.09	0.13	0.00	0.17	0.10	0.14	0.49	1.23

that the number decreases by an order of magnitude in all cases, as the pressure increased from a near vacuum to 200 Torr. The exact decrease depends on the peaks' energy as expected, since less energetic X-rays attenuate more than high-energy X-rays.

We have estimated the number of the X-rays counts reaching the detector compared to that in vacuum. Electron attenuation was estimated by Monte Carlo simulation (Figure 3a), X-ray attenuation was quantified by using analytical formulas.^[21] The electrons attenuate at small atmosphere thickness approximately directly proportional with the atmosphere thickness (which is the product of atmosphere pressure and the traversed distance, Torr-cm). X-ray attenuation is approximately exponential,^[21] with a strong dependence of the exponential factor on the X-ray energy. By combining the two effects, the estimates were in rough agreement with the experimental curves shown in Figure 7. Since no corrections were applied for electron or X-ray attenuation during the EDX analysis of the acquired data, we conclude that taking into account the effect of atmosphere on X-ray attenuation will improve the accuracy of the analysis.

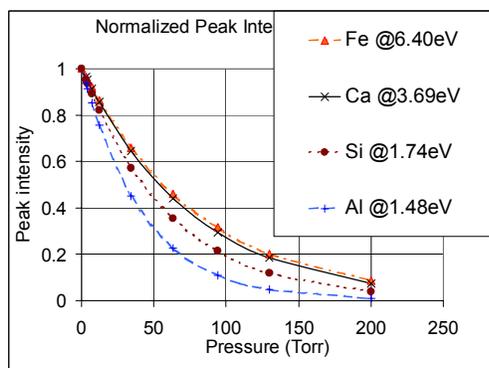


Figure 7. Normalized peak intensity vs pressure for the BCR-2 sample, for Fe, Ca, Si and Al lines.

Spectral and spatial dispersion of the incident electrons affects accuracy of the EDX analysis. Attenuation reduces the electron energy, and together with Coulomb scattering results in a non-monochromatic excitation beam. Since electrons of different energies excite X-rays with different efficiency, the effect of the lack of spectral coherence of the excitation beam will depend on beam's non-monochromaticity. The EDX software provides an option for automatic adjustment of the excitation energy to some effective value to obtain best fit to the Bremsstrahlung spectrum. The effective excitation energy was the only parameter that was automatically adjusted by the S/W during the analysis. Figure 8 shows the pressure dependence of this adjusted effective energy as a function of atmosphere thickness, and compares it with the predicted values for (a) high-energy cutoff and (b) spectral peak (i.e. energy at which the spectral distribution is maximum) for an originally monochromatic beam after it has been transmitted through the membrane and atmosphere. The simulated

spectral distributions from which the cutoff and spectral peaks were derived are shown in Figure 9. (Figure 9 shows a distribution is peaked at 17.1 keV with 17.25 keV cutoff for 20 keV electrons transmitted through a 500 nm SiN membrane and 70 Torr-cm thick atmosphere.) The cut-off is associated with energy loss by the unscattered (forward directed) electrons. The distribution peaks at energy less than the cut-off energy, the simulated profiles are broader, the peaks less pronounced, and the difference between the cut-off and spectral peak positions greater in thicker atmospheres. Note that although the dependence on

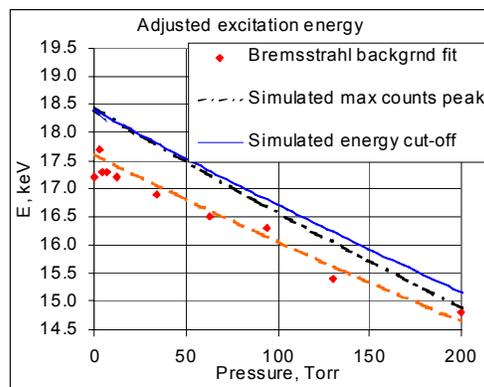


Figure 8. Effective excitation energy: The “experimental” (diamond) points were obtained by letting the SEM/EDX software adjust the electron energy to best fit the Bremsstrahlung background spectrum. The simulated energy cut-off and maximum counts peak were derived from the Monte-Carlo simulated spectral distributions such as in Figure 7.

pressure is similar, the Bremsstrahlung-fit energy is somewhat lower than the two simulated energies, attributed to the fact that the Bremsstrahlung radiation is contributed by deceleration of all, including low energy electrons. The

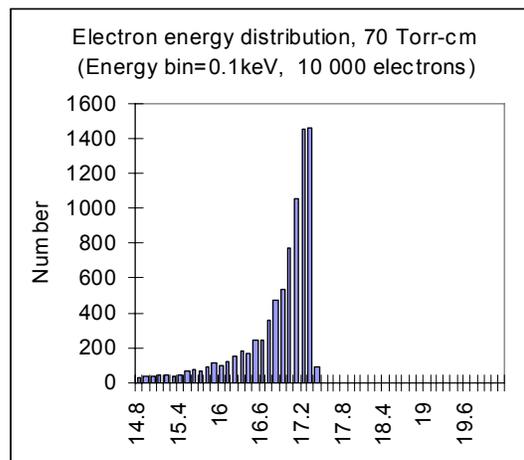


Figure 9. The simulated spectral distribution for the originally excitation electrons at 20 keV, transmitted through a 500 nm thick SiN membrane and 70 Torr-cm atmosphere.

relatively good agreement between the derived and certified compositions in Table 1 is due to the fact that the spectral distribution remains strongly peaked (at least until 90 Torr-cm, see Figure 9).

6. THE EFFECT OF THE XRF DETECTOR

The fidelity of the acquired spectra depends on spectral resolving power of the XRF detector. This could be seen by comparing the XRF spectra excited in SEM using the built-in, liquid nitrogen cooled (high resolution) SiLi detector, with those excited in the environmental chamber using the Peltier-cooled Amptek detector. Using the encapsulated 10 keV electron gun in our previous work^[2,3], we have compared the excited spectra in the Earth atmosphere to those excited in the SEM acquired using both the SiLi and Amptek detector. Whereas the X-ray transition lines were observed at the same locations (as they should) in all cases, the peaks were best resolved, due to the greater sensitivity, narrower FWHM, and the thinner polymer window when using the SiLi detector. For the Amptek detector, line-width was broadened due to the comparatively poor (253 eV at 5.9 keV) FWHM and the thicker, 12 μm thick Be window, with additional broadening observed when used in the Earth atmosphere.

For our most recent work, we used a newly purchased Amptek detector with a narrower FWHM (1.49 eV) and thinner detector window (8 μm Be). The detector system includes a Detector Power Supply, Pulse Shaping Amplifier (PSA) & Multi Channel Analyzer (MCA) all built into a single package just slightly larger than our old detector but without bulky external electronics modules. The effect of the improved detector on the acquired spectra is demonstrated in Fig 10, which shows the spectra for the Gabbro mineral (Norite) sample from the Stillwater Complex, Sweet Grass County Montana. Note that the Mg, Al, and Si lines (which were convoluted using the old detector) were resolved using the new detector. EDX analysis of a better resolved spectrum will determine the elemental abundance with a greater accuracy.

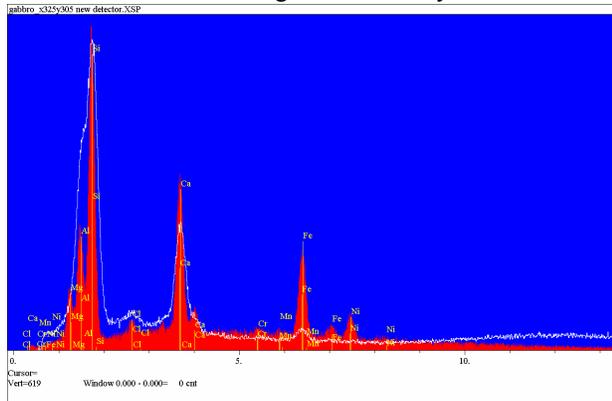


Figure 10. Comparison of the acquired XRF spectra for the Gabbro (Norite) from the Stillwater Complex, Sweet Grass County Montana using the old (thin white line) and the new (solid red line) Amptek detector

The spectral fidelity is expected to improve further with the planned use of the Ketek detector (that was used on the 2003 Mars Exploration Rover (MER) mission)^[22] in a flight version of the instrument.

7. RESOLVING MINERAL GRAINS

To test our ability to resolve mineral “grains” in the rock and differences in their respective compositions, the encapsulated 20 keV tube was also used to excite XRF spectra from a number of complex rocks. A new environmental chamber was built to perform these experiments, to facilitate working distances as short as 1 mm. A moving stage was incorporated into the chamber and mineral samples containing mm-scale size grains of unknown composition were placed on top of it producing beam scanning.

Figure 11 shows a Gabbro (Norite) sample from the Stillwater Complex, Sweet Grass County Montana, which contained mineral grains of 1 to 3 mm in size. The stage was stepped in 0.5 mm increments underneath the electron beam, and XRF spectra acquired at each step. The AEXS beam differentiated the grains with about 1.5 mm spatial resolution. Specifically, as Figure 11 shows, Mg & Fe rich areas were differentiated from Ca & Al rich areas in the

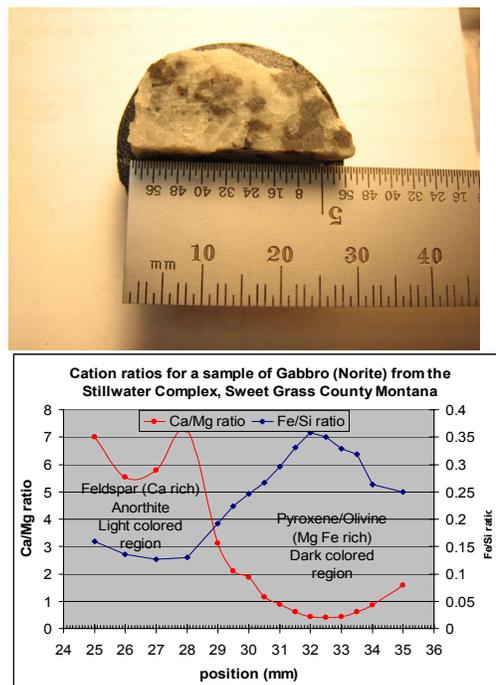


Fig 11. The AEXS instrument was used to resolve composition of grains in Gabbro (Norite) sample from the Stillwater Complex, Sweet Grass County Montana, with 1.5 mm spatial resolution. (a) The Gabbro sample contains grains of 1-3 mm in size. (b) The AEXS differentiated the Mg & Fe rich areas from the Ca & Al rich areas. Resolving the elemental composition spatially may give clues about sample’s geologic origin.

rock. This is the first demonstration of the ability of any XRF instrument to map surface elemental composition with better than several cm-scale spatial resolution. Other XRF instruments (APXS, flown on Pathfinder and MER) or the CheMin (selected for MSL mission), are essentially bulk analysis instruments. Resolving the elemental composition spatially may give clues about sample's geologic origin.

8. INSTRUMENT HEAD FOR INTEGRATION ON A MOBILE PLATFORM

The developmental plans for the AEXS include assembly of an instrument head to be mounted on a mobile platform. When implemented on a rover arm, AEXS would be able to determine elemental composition of freshly exposed rock surfaces or soil grains on planetary surfaces, as a part of a payload that would also include a visual light camera capable of imaging the area being analyzed. Figure 12 shows a rendering of the envisioned instrument head. The head integrates a Walton-Cockroft high voltage multiplier that delivers voltages to the gun's four electrodes, and to the filament heating power supply. The power supply is being developed in several stages, including design and fabrication of the electronic boards, development of the dielectric housing envelope (necessitated by low electrical strength of the Mars atmosphere pressure), and instrument design for low temperature operation, in cooperation with Aerosino Inc.

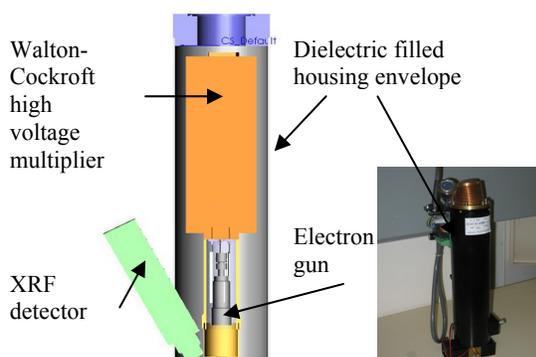


Fig 12. AEXS Instrument head concept. The Walton-Cockroft high voltage multiplier delivers voltages to the gun and to the filament heating power supply.

9. CONCLUSIONS

AEXS is an *in situ* instrument for the determination of surface elemental composition using energy-dispersive XRF analysis, of samples in planetary atmosphere with no or little sample preparation. The AEXS instrument head requires no external vacuum support. The laboratory prototype has been used to determine elemental composition for several mineral standards in simulated atmospheres in

the environmental chamber with a good agreement (4%) obtained for samples in up to 90 Torr-cm thick atmosphere. It has also been used to detect XRF spectra from inhomogeneous rocks with mineral grains of unknown composition; specifically it has been used to resolve grains in Gabbro (Norite) sample from the Stillwater Complex, Sweet Grass County Montana, with 1.5 mm spatial resolution. Using the prototype instrument, Mg & Fe rich areas were differentiated from Ca & Al rich areas. This is the first demonstration of the ability of any XRF instrument to map elemental composition with better than several cm-scale spatial resolution. Other XRF instruments (APXS, flown on MER) or the CheMin (selected for MSL mission), are essentially bulk analysis instruments. Resolving the elemental composition spatially may give clues about samples geological origin.

The spectrum analysis time was 100 seconds, and the XRF spectra analyzed using a commercial SEM/EDX software package with no corrections for the non-monochromatic beam included in the analysis, with a good agreement obtained up to about 90 Torr-cm atmosphere thickness. Shorter working distances will allow operation at commensurately higher pressures. Flushing the working distance region with He, working in reduced pressure atmospheres on Mars or other NASA mission destinations, or by including corrections to the EDX code that account for loss of energy and spectral coherence for the excitation electrons and X-ray absorption, may enable operation at longer working distances in thicker atmospheres.

Table 2. Merits of electron-induced excitation with other *in-situ* excitation methods of XRF (*assumes CNT-emitter primary source)

Property for XRF excitation	CNT-array emitters*	XRF/XRD*	APXS (MER)
Excitation particles	Electrons	X-ray photons	α -particles
Spectrum acquisition time	< 30 sec	5 min/30min	0.5 hour
Energy per acquired spectrum	< 30 J	300 J/2000 J	500 J (includes electronics)
Scanning ability	Electronic	Mechanical	None
Spatial resolution	Several ten μm^2 to cm^2	$\sim \text{mm}^2$ - cm^2	$\sim \text{cm}^2$
Can be turned off during operation	Yes	Yes	No: radioactive

For our future work, we are planning to replace the thermionic emitters of the commercially available electron guns with Carbon-nanotube-based field-emitters, greatly simplifying the power supply architecture. The simplification will result in a significantly lower power consumption as well as additional savings in mass, and a

compact, portable instrument for performing rapid analysis at medium (several hundreds micrometers to several cm, depending on atmosphere thickness) spatial resolution. The potential for miniaturization addresses the need of planetary missions for *in situ* analysis tools with the ability to resolve mineral grains on intermediate spatial scale, complementary to bulk-analysis instruments such as the APXS used in the MER mission. Table 2 summarizes the merit parameters for the AEXS and compares them with the APXS and the proposed XRF/XRD instrument.

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12. BIOGRAPHY

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